

FORM PTO-1390 (Modified)  
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

## TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

1001-0010

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

To Be Assigned **09/720122**

INTERNATIONAL APPLICATION NO

**PCT/JP00/02752**

INTERNATIONAL FILING DATE

**26-April-2000**

PRIORITY DATE CLAIMED

**27-April-1999**

TITLE OF INVENTION

**Glass Etching Composition and Method for Frosting Using the Same**

APPLICANT(S) FOR DO/EO/US

**MIWA, Hiroshi**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

1. Copy of the Published PCT Application, No. WO00/64828;
2. Copy of Form PCT/IB/304;
3. Copy of Form PCT/IB/308; and
4. Verified Statement Claiming Small Entity Status.

U.S. APPLICATION NO. IF KNOWN, SEE 37 CFR 1.53 <b>09/720122</b> To Be Assigned		INTERNATIONAL APPLICATION NO. <b>PCT/JP00/02752</b>		ATTORNEY'S DOCKET NUMBER <b>1001-0010</b>	
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21. The following fees are submitted:

BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/>	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . .	\$970.00			
<input checked="" type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . .	\$840.00			
<input type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . .	\$690.00			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . .	\$670.00			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . .	\$96.00			
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$840.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<b>\$0.00</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	22 - 20 =	2	x \$18.00	<b>\$36.00</b>	
Independent claims	2 - 3 =	0	x \$78.00	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$876.00</b>	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).			<input checked="" type="checkbox"/>	<b>\$438.00</b>	
<b>SUBTOTAL =</b>				<b>\$438.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).			+	<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$438.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).			<input type="checkbox"/>	<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$438.00</b>	
				Amount to be:	\$
				refunded	
				charged	\$

☒ A check in the amount of **\$438.00** to cover the above fees is enclosed.

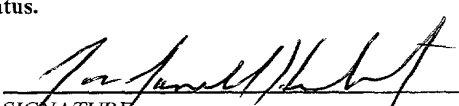
☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **50-0622** A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**SHANKS & HERBERT**  
 TransPotomac Plaza  
 1033 North Fairfax Street, Suite 306  
 Alexandria, VA 22314  
 (703) 683-3600  
 (703) 683-9875 (facsimile)

  
 SIGNATURE

**Toni-Junell Herbert**  
 NAME

**34,348**  
 REGISTRATION NUMBER

**12/21/00**  
 DATE

**STATEMENT CLAIMING SMALL ENTITY STATUS  
(37 CFR 1.9(f) & 1.27(b))--INDEPENDENT INVENTOR**

Docket Number (Optional)

Applicant, Patentee, or Identifier: \_\_\_\_\_

Application or Patent No.: \_\_\_\_\_

Filed or Issued: \_\_\_\_\_

Title: GLASS ETCHING COMPOSITION AND METHOD FOR FROSTING USING THE SAME

As a below named inventor, I hereby state that I qualify as an independent inventor as defined in 37 CFR 1.9(c) for purposes of paying reduced fees to the Patent and Trademark Office described in:

- ☒ the specification filed herewith with title as listed above.  
☐ the application identified above.  
☐ the patent identified above.

I have not assigned, granted, conveyed, or licensed, and am under no obligation under contract or law to assign, grant, convey, or license, any rights in the invention to any person who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e)

Each person, concern, or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

- ☒ No such person, concern, or organization exists.  
☐ Each such person, concern, or organization is listed below.

Separate statements are required from each named person, concern, or organization having rights to the invention stating their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate (37 CFR 1.28(b))

<p>Hiroshi MIWA</p> <p>NAME OF INVENTOR</p> <p><i>Hiroshi Miwa</i></p> <p>Signature of inventor</p> <p><u>10 December 2000</u></p> <p>Date</p>	<p>NAME OF INVENTOR</p> <p>Signature of inventor</p> <p>Date</p>	<p>NAME OF INVENTOR</p> <p>Signature of inventor</p> <p>Date</p>
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## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

MIWA

Appl. No.: To be Assigned

Filed: Herewith

For: GLASS ETCHING COMPOSITION AND  
METHOD FOR FROSTING USING THE SAME

Art Unit: To Be Assigned

Examiner: To Be Assigned

Atty. Docket: 1000-0010

**Preliminary Amendment**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, Applicant herewith respectfully requests the following amendments:

IN THE CLAIMS:

Please cancel claim 13.

1. A glass etching [liquid] composition [comprises] comprising 1 to 10 w/v % of fluoride, 20 to 80 v/v % of water and 20 to 80 v/v % of a water-miscible organic solvent.

2. The glass etching composition as claimed in claim 1, [wherein said] further comprising a gelling agent[s are added].

3. The glass etching composition as claimed in claim 1 [or 2], further comprising [wherein] sucrose [is added] as a stabilizer.

4. The glass etching composition as claimed in [any one of] claim[s] 1 [to 3], further comprising a [wherein said] surfactant[s are added].

5. The glass etching composition as claimed in [any one of] claim[s] 1 [to 4], wherein at least one of acetic acid, citric acid and phosphoric acid, and [said] a buffer thereof are added to adjust a pH of the glass etching composition.

6. The glass etching composition as claimed in [any one of] claim[s] 1 [to 5], further comprising a [wherein said] dye [is added] to color[ed] the composition.

7. The glass etching composition as claimed in [any one of] claim[s] 1 [to 6], wherein said fluoride is at least one compound selected from the group consisting of sodium fluoride, potassium fluoride, ammonium fluoride, sodium bifluoride, potassium bifluoride and ammonium bifluoride.

8. The glass etching composition as claimed in [any one of] claim[s] 1 [to 7], wherein said water is selected from the group consisting of tap water, ion exchange water, distilled water, ground water, spring water, filtrate water and a mixture of two or more thereof.

9. The glass etching composition as claimed in [any one of] claim[s] 1 [to 8], wherein said water-miscible solvent is at least one compound selected from glycerin, [and the group consisting of] a glycol, [such as methyl glycol, ethyl glycol, methylene glycol, ethylene glycol, propylene glycol, dimethylene glycol, diethylene glycol, dipropylene glycol, polymethylene glycol and polyethylene glycol, and the group consisting of] a glycol ether and an alcohol [such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, dipropylene

glycol monoisopropyl ether and dipropylene glycol monobutyl ether, and the group consisting of a alcohol such as methanol, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, 1,2-ethane diol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,2,3-propane triol, 1,2,6-hexane triol and sorbitol].

--10. The glass etching composition as claimed in claim 9, wherein said glycol is methyl glycol, ethyl glycol, methylene glycol, ethylene glycol, propylene glycol, dimethylene glycol, diethylene glycol, dipropylene glycol, polymethylene glycol or polyethylene glycol.--

--11. The glass etching composition as claimed in claim 9, wherein said glycol ether is ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene monoethyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monoisopropyl ether or dipropylene glycol monobutyl ether.--

--12. The glass etching composition as claimed in claim 9, wherein said alcohol is methanol, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, 1,2-ethane diol, 1,2-propane triol, 1,2,6-hexane triol or sorbitol.--

13[10]. The glass etching composition as claimed in [any one of] claim [1 to 9] 2, wherein said gelling agent is at least one compound selected from the group consisting of hydroxypropyl cellulose, hydroethyl cellulose, methyl cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, sodium arginate, arabic gum, tragacanth gum, xanthum gum, bentonite, veegum, gelatin, bengl gelatin, polyacrylate, polyacryl amide, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetate, an acrylate polymer, an isobutyl maleic

acid copolymer, an acrylic acid/methacrylic acid copolymer, an acrylic acid/maleic acid copolymer and [variants] an equivalent thereof.

14[11]. The glass etching composition as claimed [in any one of] claim[s 1 to 10] 4, wherein said surfactant is [at least one compound selected from the group consisting of] an anionic surfactant, [such as dodecylbenzene sodium sulfonate, an alkylbenzene sodium sulfonate, lignine calcium sulfonate, a perfluoroalkyl sulfonate, a perfluoroalkyl carboxylate and a perfluoroalkyl phosphate, and the group consisting of] an non-ionic surfactant, [such as polyoxyethylene acetyl ether, polyoxyethylene lauryl ether, polyoxyethylene oleil ether, polyoxyethylene stearyl ether, a polyoxyethylene alkyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, sorbitan laurate, sorbitan palmitate, sorbitan oleate, sorbitan stearate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monooleate and polyoxyethylene sorbitan monostearate, and the group consisting of an ampholytic surfactant such as a dimethylalkyl betain, a alkyl glycine, amide betaine, imidazoline, a perfluoroalkylamino sulfonate, a perfluoroalkyl betaine, and the group consisting of a cationic surfactant such as octadecyldimethylbenzylammonium chloride, a alkyldimethylbenzylammonium chloride, tetradecyldimethylbenzykammonium chloride, dioleyldimethylammonium chloride, octadecyltrimethylammonium chloride, a alkyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, a octadecylamine acetate, a hexadecylamine acetate, a perfluoroalkyltrimethylammonium salt and a perfluoroalkyl quaternary ammonium salt] an amphoteric surfactant or a cationic surfactant.

--15. The glass etching composition as claimed in claim 14, wherein said an anionic surfactant is dodecylbenzene sodium sulfonate, an alkylbenzene sodium sulfonate, lignin calcium sulfonate, a perfluoroalkyl sulfonate, a perfluoroalkyl carboxylate or a perfluoroalkyl phosphate.--

--16. The glass etching composition as claimed in claim 14, wherein said non-ionic surfactant is polyoxyethylene acetyl ether, polyoxyethylene lauryl ether, polyoxyethylene oleyl ether, polyoxyethylene stearyl ether, a polyoxyethylene alkyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, sorbitan laurate, sorbitan palmitate, sorbitan oleate, sorbitan stearate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monooleate or polyoxyethylene sorbitan monostearate.--

--17. The glass etching composition as claimed in claim 14, wherein said amphoteric surfactant is a dimethylalkyl betain, a alkyl glycine, amide betaine, imidazoline, a perfluoroalkylamino sulfonate or a perfluoroalkyl betaine.--

--18. The glass etching composition as claimed in claim 14, wherein said cationic surfactant is octadecyldimethylbenzylammonium chloride, a alkyl dimethyl benzylammonium chloride, tetradecyldimethylbenzylammonium chloride, dioleyldimethylammonium chloride, octadecyltrimethylammonium chloride, a alkyltrimethylammonium chloride, dodecyl-trimethylammonium chloride, hexadecyltrimethylammonium chloride, octadecylamine acetate, hexadecylamine acetate, a perfluoroalkyl-trimethylammonium salt and a perfluoroalkyl quaternary ammonium salt.--



19[12]. A frosting method for frosting a glass surface by using a [the] glass etching [liquid] composition, [for a glass surface] comprising the steps of:

- (a) cleaning a glass surface with a cleaning agent and wiping the glass dry,
- (b) masking a portion of [protecting] the glass surface [by masking on to a portion] where etching is not required,
- (c) etching [coating] the glass surface with the glass etching [liquid] composition as claimed in [any one of] claim[s] 1[, 3, 4, 5, 6, 7, 8, 9 and 11] by immersing, [or] spraying [to etch the glass surface] or coating,
- (d) washing [cleaning] the glass surface [again,] and removing the glass etching composition [and the masking] therefrom.

--20. The frosting method as claimed in claim 19, wherein the glass surface is coated by applying with a brush or squeezing from a tube.--

21[14]. The frosting method [for a glass surface] as claimed in claim [12 or 13] 19, wherein said cleaning agent is [selected from] water, a soap, a household cleanser or a household detergent.

22[15]. The frosting method [for a glass surface] as claimed in [any one of] claim[s] 12 to 14] 19, wherein said masking is made by an oily pen, an oily paint, a resin paint, an acrylic paint, a masking tape, a seal, or a silk screen printing method[, or other printing methods].

REMARKS

Applicant confirms that the amendments made herein do introduce new material not previously discussed in the patent application. It is respectfully requested that the Examiner enter these amendments prior to examining the application on its merits.

Date:

12/21/1-

Respectfully submitted,

SHANKS & HERBERT

By:

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GLASS ETCHING COMPOSITION AND  
METHOD FOR FROSTING USING THE SAME

**FIELD OF THE INVENTION**

The present invention relates to a glass etching liquid or gel composition comprising ammonium bifluoride, a water-miscible organic solvent and water, in which no hydrofluoric acid is contained and a concentration of the ammonium bifluoride is relatively low. Further, the present invention relates to a frosting method therewith for a glass surface, whereby a glass surface in any shapes, i.e., flat, curved, or tubular shapes is easily frosted.

**BACKGROUND OF THE INVENTION**

A conventional etching composition for frosting a glass surface typically contains hydrofluoric acid, sulfuric acid or nitric acid. In recent years, an attempt has been made to avoid the use of hydrofluoric acid which has been a fundamental cause for the problems of health hazard and of environmental pollution.

For example, Japanese Patent Publication No. Hei 8-5694 discloses a glass etching composition comprising ammonium bifluoride, water, ferric chloride, sucrose and glycerin.

However, the glass etching composition needs 25 to 35% by weight of ammonium bifluoride, and further comprises 90% by weight of glycerin as a solvent, 12 to 26% by weight of sucrose as a flow modifier and 3.5 to 7.5% by weight of ferric chloride as an activator.

Glycerin may be used to form a film on a glass surface. Large amounts of glycerin and ferric chloride contained therein inhibit ammonium bifluoride from diffusing, resulting in a remarkably lowered etching reactivity. Such glass etching composition has very high viscosity, and therefore cannot provide a precise pattern and design on the glass surface. In addition, a large amount of ammonium bifluoride may cause health damages. Accordingly, the glass etching composition cannot be conveniently used, and is not suitable for daily application, but for special application.

The present invention provides a glass etching composition, which solves the above mentioned problems, and also provides a frosting method therewith for a glass surface.

#### SUMMARY OF THE INVENTION

According to the present invention, a glass etching liquid composition comprising 1 to 10 weight/volume % (hereinafter referred to as w/v %), preferably 2 to 5 w/v % of fluoride, 20 to 80 volume/volume % (hereinafter referred to as v/v %), preferably 20 to 50 v/v % of water and 20 to 80 v/v %, preferably 50 to 80 v/v % of water-miscible organic solvent is provided.

The glass etching composition is gelled by adding a gelling agent.

The glass etching composition gelled or not gelled may further contain sucrose as a stabilizer.

The glass etching composition gelled or not gelled may further contain surfactants.

The glass etching composition gelled or not gelled may further contain at least one of acetic acid, citric acid and phosphoric acid, and a buffer thereof to adjust a pH.

The glass etching composition gelled or not gelled may be colored with a dye.

The fluoride in the glass etching composition gelled or not gelled is at least one compound selected from the group consisting of sodium fluoride, potassium fluoride, ammonium fluoride, sodium bifluoride, potassium bifluoride and ammonium bifluoride.

The water in the glass etching composition gelled or not gelled is selected from the group consisting of tap water, ion exchange water, distilled water, ground water, spring water, filtrate water and a mixture of two or more thereof.

The water-miscible organic solvent in the glass etching composition gelled or not gelled is at least one compound selected from glycerin, and the group consisting of a glycol such as methyl glycol, ethyl glycol, methylene glycol, ethylene glycol, propylene glycol, dimethylene glycol, diethylene glycol, dipropylene glycol, polymethylene glycol and polyethylene glycol, and the group consisting of a glycol ether such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monoisopropyl ether and dipropylene glycol monobutyl ether, and the group consisting of a alcohol such

as methanol, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, 1,2-ethane diol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,2,3-propane triol, 1,2,6-hexane triol and sorbitol.

The gelling agent in the glass etching composition gelled is at least one compound selected from the group consisting of hydroxypropyl cellulose, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, sodium arginate, arabic gum, tragacanth gum, xanthum gum, bentonite, veegum, gelatin, bengl gelatin, polyacrylate, polyacryl amide, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetate, an acrylate polymer, an isobutyl maleic acid copolymer, an acrylic acid / methacrylic acid copolymer, an acrylic acid / maleic acid copolymer and variants thereof.

The surfactant in the glass etching composition gelled or not is at least one compound selected from the group consisting of an anionic surfactant such as dodecylbenzene sodium sulfonate, an alkylbenzene sodium sulfonate, lignine calcium sulfonate, a perfluoroalkyl sulfonate, a perfluoroalkyl carboxylate and a perfuloroalkyl phosphate, and the group consisting of an non-ionic surfactant such as polyoxyethylene acetyl ether, polyoxyethylene lauryl ether, polyoxyethylene oleil ether, polyoxyethylene stearyl ether, a polyoxyethylene alkyl ether, polyoxyethylene octyl-phenyl ether, polyoxyethylene nonylphenyl ether, sorbitan laurate, sorbitan palmitate, sorbitan oleate, sorbitan stearate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan mono-

palmitate, polyoxyethylene sorbitan monooleate and polyoxyethylene sorbitan monosteate, and the group consisting of an ampholytic surfactant such as a dimethylalkyl betain, a alkyl glycine, amide betaine, imidazoline, a perfluoroalkylamino sulfonate, a perfluoroalkyl betaine, and the group consisting of a cationic surfactant such as octadecyldimethylbenzylammonium chloride, a alkyl dimethylbenzylammonium chloride, tetradecyldimethylbenzylammonium chloride, dioleyldimethylammonium chloride, octadecyl trimethylammonium chloride, a alkyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, a octadecylamine actate, a hexadecylamine acetate, a perfluoroalkyltrimethylammonium salt and a perfluoroalkyl quaternary ammonium salt.

The glass etching liquid composition of the present invention is preferably used to frost glass articles. After cleaning on the glass surface by flushing with a cleaning agent and wiping the glass dry, the glass surface where etching is not required is optionally protected by masking. The glass is coated with the glass etching composition by immersing or spraying. After completion the frosting treatment, the glass is cleaned again with water to remove the residual etching composition and the masking therefrom.

The glass etching gel composition of the present invention is preferably used to frost glass articles. After cleaning on the glass surface by flushing with the cleaning agent and wiping the glass dry, the glass surface where etching is not required is optionally protected by masking. The glass is coated with the glass

etching composition by immersing, applying with a brush or squeezing from a tube. After completion the frosting treatment, the glass is cleaned again with water to remove the residual etching composition and the masking therefrom.

In the frosting method for a glass surface, the cleaning agent is selected from water, a soap, a household cleanser or a household detergent.

In the frosting method for a glass surface, the masking is made by an oily pen, an oily paint, a resin paint, an acrylic paint, a masking tape, a seal, a silk screen printing method or other printing methods.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Other features of this invention will become apparent in the course of the following description of exemplary embodiments, which are given for illustration of the invention and are not intended to be limiting thereof.

##### Example 1

An aqueous solution was prepared by dissolving 3 to 30 w/v % of ammonium bifluoride and was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 2 parts of propylene glycol. Accordingly, the final glass etching composition consisted 1 to 10 w/v % of ammonium bifluoride.

Specifically, the aqueous solution was prepared by dissolving 12 g of ammonium bifluoride in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue



by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 200 ml of propylene glycol was added, whereby 300 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride, 33.3 v/v % of water and 66.7 v/v % of propylene glycol.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness; a glass cup having a size of 50 mm in outer diameter, 95 mm in height and 1 mm in thickness; and a mirror having a size of 900 mm in outer diameter were frosted as follows: the glass plate, the glass cup and the mirror were washed with tap water and the tap water was wiped off. Then, the glass plate, the glass cup and the mirror were masked by painting a desired area with a blue oily pen and were immersed in the glass etching composition for 5 to 15 minutes. Thereafter, the glass plate, the glass cup and the mirror were removed therefrom and were washed with tap water. Thus, the areas not masked were frosted.

A frosted image density on the glass surface increased, as a concentration of ammonium bifluoride increased, which led to a shortened immersion time. It has been found that sufficient density and uniformity of the frosted image was obtained by immersing the glass surface in 3 to 5 w/v % of ammonium bifluoride for 10 minutes. If more than 5 w/v % of ammonium bifluoride is used, an excellent frosted image density cannot be obtained because the glass surface is partly acid polished. Compared to glycols, glycerin provides a decreased frosted image density.

## Example 2

An aqueous solution was prepared by dissolving 12 w/v % of ammonium bifluoride and was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 1 to 4 parts of propylene glycol, ethylene glycol or glycerin. Accordingly, the final glass etching composition consisted 2.4 to 6 w/v % of ammonium bifluoride.

Specifically, the aqueous solution was prepared by dissolving 12 g of ammonium bifluoride in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 300 ml of glycerin was added, whereby 400 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 3 w/v % of ammonium bifluoride, 25 v/v % of water and 75 v/v % of glycerin.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness; a glass cup having a size of 50 mm in outer diameter, 95 mm in height and 1 mm in thickness; and a mirror having a size of 900 mm in outer diameter were frosted as follows: the glass plate, the glass cup and the mirror were washed with tap water and the tap water was wiped off. Then, the glass plate, the glass cup and the mirror were masked by painting a desired area with a blue oily pen and were immersed in the glass etching composition for 10 minutes. Thereafter, the glass plate, the glass cup and the mirror were

removed therefrom and were washed with tap water. Thus, the areas not masked were frosted.

It has been found that sufficient density and uniformity of the frosted image on the glass surface was obtained when a volume ratio of the aqueous solution to glycols or glycerin was 1:2 to 1:3. Compared to glycols, glycerin provides a decreased frosted image density.

### Example 3

An aqueous solution was prepared by dissolving 16 w/v % of ammonium bifluoride and was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 3 parts of one or two more of water-miscible solvents selected from propylene glycol, polyethylene glycol 200 (an average molecular weight of about 200), polyethylene glycol 400 (an average molecular weight of about 400) and glycerin. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride.

Specifically, the aqueous solution was prepared by dissolving 16 g of ammonium bifluoride in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 200 ml of propylene glycol and 100 ml of polyethylene glycol 200 were added, whereby 400 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride, 25 v/v % of water, 50 v/v % of propylene glycol and 25 v/v % of polyethylene glycol 200.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness was frosted as follows: the glass plate was washed with tap water and the tap water was wiped off. Then, the glass plate was masked by painting a desired area with a blue oily pen and was immersed in the glass etching composition for 5 to 10 minutes. Thereafter, the glass plate was removed therefrom and was washed with tap water. Thus, the areas not masked were frosted.

A frosted image density on the glass surface decreased, as both a concentration and an average molecular weight of the polyethylene glycol increased. Polymerization degree of polyethylene glycol is not especially limited. In view of a production of the glass etching composition, it is preferred that polyethylene glycol have an average molecular weight of about 200 to 400, since such polyethylene glycol is liquid. As a concentration of glycerin increased, the frosted image density decreased, as is the case with polyethylene glycol. The same result can be obtained using diethylene glycol instead of propylene glycol.

#### Example 4

An aqueous solution was prepared by dissolving 15 w/v % of ammonium bifluoride and was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 2 to 3 parts of propylene glycol and 0 to 1 part of isopropyl alcohol or 1,2,6-hexane triol. Accordingly, the final glass etching

composition consisted 3 to 5 w/v % of ammonium bifluoride.

Specifically, the aqueous solution was prepared by dissolving 15 g of ammonium bifluoride in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 300 ml of propylene glycol and 100 ml of isopropyl alcohol were added, whereby 500 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 3 w/v % of ammonium bifluoride, 20 v/v % of water, 60v/v % of propylene glycol and 20 v/v % of polyethylene glycol 200.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness was frosted as follows: the glass plate was washed with tap water and the tap water was wiped off. Then, the glass plate was masked by painting a desired area with a blue oily pen and was immersed in the glass etching composition for 5 to 10 minutes. Thereafter, the glass plate was removed therefrom and was washed with tap water. Thus, the areas not masked were frosted.

A frosted image density on the glass surface decreased, as a concentration of the alcohols increased. The same result can be obtained using other alcohols, but it may be difficult to obtain a uniform frosted surface.

#### Example 5

An aqueous solution was prepared by dissolving 12 w/v % of ammonium bifluoride and 0 to 20 w/v % of sorbitol. The aqueous

solution was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 3 parts of propylene glycol. Accordingly, the final glass etching composition consisted 3 w/v % of ammonium bifluoride and 0 to 5 w/v % of sorbitol.

Specifically, the aqueous solution was prepared by dissolving 12 g of ammonium bifluoride and 20 g of sorbitol in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 300 ml of propylene glycol was added, whereby 400 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 3 w/v % of ammonium bifluoride, 5 w/v % of sorbitol, 25 v/v % of water and 75v/v % of propylene glycol.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness was frosted as follows: the glass plate was washed with tap water and the tap water was wiped off. Then, the glass plate was masked by painting a desired area with a blue oily pen and was immersed in the glass etching composition for 5 to 10 minutes. Thereafter, the glass plate was removed therefrom and was washed with tap water. Thus, the areas not masked were frosted.

A frosted image density on the glass surface increased, as a concentration of sorbitol in the glass etching composition increased. However, if a part of propylene glycol is replaced of other water-miscible organic solvents, the frosted image density may decreases. Thus, the frosted image density does not always

depend on the concentration of sorbitol.

#### Example 6

An aqueous solution was prepared by dissolving 12 w/v % of ammonium bifluoride and 0 to 3 v/v % or w/v % of one or two more of surfactants selected from polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyoxyethylene sorbitan monolaurate, lignin calcium sulfonate, and dodecylbenzene sodium sulfonate. The aqueous solution was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 2 parts of propylene glycol. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride and 0 to 1 v/v % or 0 to 1 w/v % of the surfactant(s).

Specifically, the aqueous solution was prepared by dissolving 12 g of ammonium bifluoride and 1.5 g of polyoxyethylene octylphenyl ether in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 200 ml of propylene glycol was added, whereby 300 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride, 0.5 w/v % of polyoxyethylene octylphenyl ether, 33.3 v/v % of water and 66.7 v/v % of propylene glycol.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness was frosted as follows: the glass plate was washed with tap water

and the tap water was wiped off. Then, the glass plate was masked by painting a desired area with a blue oily pen and was coated with the glass etching composition by spraying. Thereafter the glass plate was allowed to stand for 5 minutes and was washed with tap water. Thus, the areas not masked were frosted.

The surfactants did not significantly affect the frosted image density on the glass surface, but promoted adhering the glass etching composition to the glass surface evenly. Other surfactants can provide the same effect more or less.

#### Example 7

An aqueous solution was prepared by dissolving 12 w/v % of ammonium bifluoride and 0 to 30 w/v % of sucrose. The aqueous solution was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 2 parts of propylene glycol. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride and 0 to 10 w/v % of sucrose.

Specifically, the aqueous solution was prepared by dissolving 12 g of ammonium bifluoride and 15 g of sucrose in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 200 ml of propylene glycol was added, whereby 300 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride, 5 w/v % of sucrose, 33.3 v/v % of water and 66.7 v/v % of propylene glycol.



Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness was frosted as follows: the glass plate was washed with tap water and the tap water was wiped off. Then, the glass plate was masked by painting a desired area with a blue oily pen and was immersed in the glass etching composition for 5 to 10 minutes. Thereafter, the glass plate was removed therefrom and was washed with tap water. Thus, the areas not masked were frosted.

A frosted image density on the glass surface increased, as a concentration of sucrose in the glass etching composition increased. However, if a part of propylene glycol is replaced of other water-miscible organic solvents, the frosted image density may decreases. Thus, the frosted image density does not always depend on the concentration of sucrose.

#### Example 8

An aqueous solution was prepared by dissolving 5 to 20 w/v % of ammonium bifluoride and was colored blue by adding Brilliant Blue FCF. Then, 1 part of the aqueous solution was mixed with 1 part of propylene glycol. Accordingly, the final glass etching composition consisted 2.5 to 10 w/v % of ammonium bifluoride.

Specifically, the aqueous solution was prepared by dissolving 20 g of ammonium bifluoride in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 100 ml of propylene glycol was added, whereby 200 ml of the glass

etching composition was obtained. Accordingly, the final glass etching composition consisted 10 w/v % of ammonium bifluoride, 50 v/v % of water and 50 v/v % of propylene glycol.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness; and a glass cup having a size of 50 mm in outer diameter, 95 mm in height and 1 mm in thickness were frosted as follows: the glass plate and the glass cup were washed with tap water and the tap water was wiped off. Then, the glass plate and the glass cup were masked by painting a desired area with a blue oily pen and were immersed in the glass etching composition for 5 to 10 minutes. Thereafter, the glass plate and the glass cup were removed therefrom and were washed with tap water. Thus, the areas not masked were frosted.

A frosted image density on the glass surface increased, as a concentration of ammonium bifluoride increased, which led to a shortened immersion time. However, an excellent frosted image density sometimes cannot be obtained because the glass surface is partly acid polished.

#### Example 9

An aqueous solution was prepared by dissolving 1.5 to 15 w/v % of ammonium bifluoride and 0 to 1.5 v/v % or w/v % of one or two more of surfactants selected from polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyoxyethylene sorbitan monolaurate, lignin calcium sulfonate, and dodecylbenzene sodium sulfonate. The aqueous solution was colored blue by adding

Brilliant Blue FCF. Then, 2 parts of the aqueous solution was mixed with 1 part of propylene glycol. Accordingly, the final glass etching composition consisted 1 to 10 w/v % of ammonium bifluoride and 0 to 1 v/v % or 0 to 1 w/v % of the surfactant(s).

Specifically, the aqueous solution was prepared by dissolving 12 g of ammonium bifluoride and 1.2 g of dodecylbenzene sodium sulfonate in water. The total amount of the aqueous solution was 200 ml. The aqueous solution was colored blue by adding 0.5 mg of the Brilliant Blue FCF. To the aqueous solution 100 ml of propylene glycol was added, whereby 300 ml of the glass etching composition was obtained. Accordingly, the final glass etching composition consisted 8 w/v % of ammonium bifluoride, 0.8 w/v % of dodecylbenzene sodium sulfonate, 66.7 v/v % of water and 33.3 v/v % of propylene glycol.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness; and a glass cup having a size of 50 mm in outer diameter, 95 mm in height and 1 mm in thickness were frosted as follows: the glass plate and the glass cup were washed with tap water and the tap water was wiped off. Then, the glass plate and the glass cup were masked by painting a desired area with a blue oily pen and were immersed in the glass etching composition for 5 to 10 minutes. Thereafter, the glass plate and the glass cup were removed therefrom and were washed with tap water. Thus, the areas not masked were frosted.

A frosted image density on the glass surface increased, as a concentration of ammonium bifluoride increased, which led to a

shortened immersion time. However, the glass surfaces may be partly acid polished, and the frosted surfaces may have roughened portions. The surfactants tend to solve these problems more or less.

#### Example 10

An aqueous solution was prepared by dissolving 12 w/v % of ammonium bifluoride and was colored blue by adding Light Green SFY. Then, 1 part of the aqueous solution was mixed with 2 parts of propylene glycol. A glass etching homogeneous gel composition was prepared by adding 1 to 10 w/v % of hydroxypropyl cellulose to the glass etching composition and stirring them. Accordingly, the final glass etching composition consisted 4 w/v % of ammonium bifluoride.

Specifically, the aqueous solution was prepared by dissolving 12 g of ammonium bifluoride in water. The total amount of the aqueous solution was 100 ml. The aqueous solution was colored green by adding 0.5 mg of the Light Green SFY. To the aqueous solution 200 ml of propylene glycol was added, whereby 300 ml of the glass etching composition was obtained. A glass etching homogeneous gel composition was prepared by adding 10.5 g of hydroxypropyl cellulose to the glass etching composition and stirring them. Accordingly, the final glass etching gel composition consisted 4 w/v % of ammonium bifluoride, 33.3 v/v % of water, 66.7 v/v % of propylene glycol and 3.5 w/v % of hydroxypropyl cellulose.

Using the glass etching composition, a flat glass panel having a size of 100 mm in length, 100 mm in wide and 2 mm in thickness;

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a glass cup having a size of 50 mm in outer diameter, 95 mm in height and 1 mm in thickness; and a mirror having a size of 900 mm in outer diameter were frosted as follows: the glass plate, the glass cup and the mirror were washed with tap water and the tap water was wiped off. Then, the glass plate, the glass cup and the mirror were masked by painting a desired area with a blue oily pen and were coated with the glass etching gel composition by applying with a brush, or squeezing from a tube. Thereafter, the glass plate, the glass cup and the mirror were allowed to stand for 5 to 10 minutes and were washed with tap water. Thus, the areas not masked were frosted.

For applying the glass etching gel composition with a brush to the glass surface, it is preferred that about 1 to 3.5 w/v % of hydroxypropyl cellulose is used. For squeezing the glass etching gel composition from a tube onto the glass surface, it is preferred that about 4 w/v % or more of hydroxypropyl cellulose is used. An average viscosity of hydroxypropyl cellulose is not especially limited and, for example, is within a range of 150 to 400 mps (2% solution, at 20°C) for obtaining a sufficient frosted image density and for ease of handling. If other gelling agents are used instead of hydroxypropyl cellulose, large amounts of the gelling agents are sometimes required for providing a homogeneous gel composition. With such other gelling agents, it is hard to provide a sufficient frosted image density and a uniform frosted surface.

## FIELD OF THE INDUSTRIAL UTILITY

### (DETAILED DESCRIPTION OF THE INVENTION)

According to the present invention as claimed in claims 1, 7, 8 and 9, the glass etching composition does not contain harmful hydrofluoric acid and contains a low amount of a fluoride, i.e., 4 w/v % or less of ammonium bifluoride that provides an excellent frosted glass surface. The glass etching composition of the present invention is thus highly safety. For example, when ammonium bifluoride is orally administered to mice, a LD<sub>50</sub> value is 129 mg/kg. Based on a calculation in terms of the LD<sub>50</sub> value of ammonium bifluoride, the glass etching composition exhibits a LD<sub>50</sub> of about 3225 mg/kg. A criterion LD<sub>50</sub> value of a deterious substance is 30 to 300 mg/kg in Japan. Thus, the glass etching composition of the present invention has 10 times or more safe LD<sub>50</sub> value than the criterion LD<sub>50</sub> value.

Furthermore, when the frosting is performed using the glass etching composition of the present invention containing ammonium bifluoride, it is not required to adjust pH by adding acetic acid, citric acid and phosphoric acid, and a buffer thereof. Since ammonium bifluoride has no chance to contact with acids or alkalis excessively, a production of harmful hydrogenfluoride gas or ammonia gas can be successfully prevented. In a frosting method using a conventional glass etching composition containing fluorine, protective equipment such as goggles and a pair of rubber gloves for safety precautions is essential, and an exhauster is also required. In contrast, the glass etching composition of the

present invention can be handled by hand without requiring the exhaustor. In fact, when the glass etching composition of the present invention contacts with a skin during a frosting operation, no problems are raised.

In addition, in the glass etching composition of the present invention, a ratio of water to a water-miscible organic solvent such as glycols and glycerin is entirely different from that of the conventional composition. This allows a content of a fluoride, i.e., ammonium bifluoride to be remarkably decreased.

The glass etching composition of the present invention can etch a glass surface very gently, and form uniform and fine pits thereon. The resultant frosted surface is very smooth and is compared with a normal transparent glass surface. It is possible that any characters and graphics are printed on the frosted surface using an ink in gold, silver or other colors without losing the luster of the ink. Thus, a graceful and dignified glass surface can be obtained.

Furthermore, surfaces of very thin glass, curved glass and tubular glass, which are difficult to be frosted with the conventional frosting composition, can be frosted using the glass etching composition of the present invention.

The frosting with the etching composition of the present invention can be performed at room temperature and does not proceed acutely. Therefore, a density of the frosted surface can be adjusted by changing an etching time, i.e., 1 minute, 5 minutes, or 10 minutes. Also, the density of the frosted surface can be

adjusted by changing a concentration of a fluoride, i.e., ammonium bifluoride, by changing a ratio of water to a water-miscible organic solvent such as glycols and glycerin, or by adding other alcohols. In general, the surfactant increases wetting ability of the glass etching composition through a surface tension depression and promotes the glass etching composition to be deposited uniformly on the glass surface. In the glass etching composition of the present invention, the water-miscible organic solvent acts like a surfactant.

As described above, the glass etching liquid composition of the present invention comprises a small amount of a fluoride, i.e., ammonium bifluoride; glycols, glycerin, alcohols and surfactants that are used for cosmetics and pharmaceuticals; and sucrose that is used for foods. The glass etching gel composition of the present invention comprises the glass etching liquid composition and a gelling agent such as hydroxypropyl cellulose that is used for cosmetics and pharmaceuticals. Advantageously, the glass etching composition of the present invention solves environmental and health hazard problems, which are the most significant problems in the conventional glass etching composition containing fluorine.

The glass etching composition of the present invention is free from hydrofluoric acid, sulfuric acid, nitric acid and hydrochloric acid. Thus, the glass etching composition can be safely used in various printing methods including a silk screen printing method that is suitable for etching a glass surface to provide a pattern, a picture and a character. Further, a portion of the picture, the



pattern and the character on a glass surface can be frosted by masking with a masking tape, a self-made seal, an oily pen, an oil paint, a resin paint and an acrylic paint.

In summary, the glass etching composition of the present invention can frost a glass surface having any of flat, curved, and tubular shapes, and provide safely and easily a picture, a pattern and a character on a portion of the glass surface by masking, without causing environmental pollution.

Furthermore, neither special pretreatment nor aftertreatment is needed for the frosting with the glass etching composition of the present invention.

The glass etching composition of the present invention has heat resistance, moisture resistance, resistance to ultraviolet ray and weather resistance, and therefore can be used repeatedly. A water phase and a water-miscible organic solvent phase in the glass etching composition of the present invention can be separated by filtration with a special filter paper, whereby the water phase containing a degraded fluoride is discarded, and the water-miscible organic solvent phase can be recovered and recycled.

According to the present invention as claimed in claims 2 to 10, the glass etching gel composition having various viscosities can be prepared by changing a concentration of the gelling agent. The gelling agent promotes an adhesion of the glass etching composition to a glass surface, resulting in an excellent frosted surface.

According to the present invention as claimed in claim 3,

sucrose contributes to stabilize the glass etching composition.

According to the present invention as claimed in claims 4 and 11, the surfactant increases wetting ability of the glass etching composition through a surface tension depression and promotes the glass etching composition to be deposited uniformly on the glass surface upon frosting with a spray.

According to the present invention as claimed in claim 5, acetic acid and a buffer thereof adjusts a pH of the glass etching composition to provide stability and ease of use.

According to the present invention as claimed in claim 6, the glass etching composition is colored with the dye. The dye also works as a safety marker. When the glass etching composition is discarded by diluting it with water, a color of the dye diluted is given as an indication of the safe concentration. Any water-soluble dyes can be used.

According to the present invention as claimed in claim 12, a desired pattern and design can be easily produced by immersing a masked glass surface into the glass etching composition or coating a masked glass surface with the glass etching composition, and washing off the composition. An artistic glass surface can be made.

According to the present invention as claimed in claim 13, the glass etching gel composition can be coated by applying with a brush, or squeezing from a tube, whereby a desired pattern and design can be easily produced on a glass surface. Such glass etching gel composition is easily stored and handled.

According to the present invention as claimed in claim 14,

after etching, the glass etching liquid or gel composition containing a fluoride adhered to a glass surface can be easily and entirely washed off with water.

According to the present invention as claimed in claim 15, a wide variety of patterns and designs can be easily and precisely produced by masking with an oily pen, an oily paint, an acrylic paint, a masking tape and a seal, or by a silk screen printing method and other printing methods. Artistic values of the glass can be further enhanced.

What is claimed is:

1. A glass etching liquid composition comprises 1 to 10 w/v %, of fluoride, 20 to 80 v/v % of water and 20 to 80 v/v % of water-miscible organic solvent.
2. The glass etching composition as claimed claim 1, wherein said gelling agents are added.
3. The glass etching composition as claimed claim 1 or 2, wherein sucrose is added as a stabilizer.
4. The glass etching composition as claimed in any one of claims 1 to 3, wherein said surfactants are added.
5. The glass etching composition as claimed in any one of claims 1 to 4, wherein at least one of acetic acid, citric acid and phosphoric acid, and said buffer thereof are added to adjust a pH.
6. The glass etching composition as claimed in any one of claims 1 to 5, wherein said dye is added to colored the composition.
7. The glass etching composition as claimed in any one of claims 1 to 6, wherein said fluoride is at least one compound selected from the group consisting of sodium fluoride, potassium fluoride, ammonium fluoride, sodium bifluoride, potassium bifluoride and ammonium bifluoride.
8. The glass etching composition as claimed in any one of claims 1 to 7, wherein said water is selected from the group consisting of tap water, ion exchange water, distilled water, ground water, spring water, filtrate water and a mixture of two or more thereof.
9. The glass etching composition as claimed in any one of claims

1 to 8, wherein said water-miscible solvent is at least one compound selected from glycerin, and the group consisting of a glycol such as methyl glycol, ethyl glycol, methylene glycol, ethylene glycol, propylene glycol, dimethylene glycol, diethylene glycol, dipropylene glycol, polymethylene glycol and polyethylene glycol, and the group consisting of a glycol ether such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monoisopropyl ether and dipropylene glycol monobutyl ether, and the group consisting of a alcohol such as methanol, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, 1,2-ethane diol, 1,2-propane diol, 1,3-propane diol, 1,4-butane diol, 1,2,3-propane triol, 1,2,6-hexane triol and sorbitol.

10. The glass etching composition as claimed in any one of claims 1 to 9, wherein said gelling agent is at least one compound selected from the group consisting of hydroxypropyl cellulose, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, sodium arginate, arabic gum, tragacanth gum, xanthum gum, bentonite, veegum, gelatin, bengl gelatin, polyacrylate, polyacryl amide, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetate, an acrylate polymer, an isobutyl maleic acid copolymer, an acrylic acid / methacrylic acid copolymer, an acrylic acid / maleic acid copolymer and variants

thereof.

11. The glass etching composition as claimed in any one of claims 1 to 10, wherein said surfactant is at least one compound selected from the group consisting of an anionic surfactant such as dodecylbenzene sodium sulfonate, an alkylbenzene sodium sulfonate, lignine calcium sulfonate, a perfluoroalkyl sulfonate, a perfluoroalkyl carboxylate and a perfluoroalkyl phosphate, and the group consisting of an non-ionic surfactant such as polyoxyethylene acetyl ether, polyoxyethylene lauryl ether, polyoxyethylene oleil ether, polyoxyethylene stearyl ether, a polyoxyethylene alkyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, sorbitan laurate, sorbitan palmitate, sorbitan oleate, sorbitan stearate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monooleate and polyoxyethylene sorbitan monostearate, and the group consisting of an ampholytic surfactant such as a dimethylalkyl betain, a alkyl glycine, amide betaine, imidazoline, a perfluoroalkylamino sulfonate, a perfluoroalkyl betaine, and the group consisting of a cationic surfactant such as octadecyldimethylbenzylammonium chloride, a alkyldimethyl benzylammonium chloride, tetradecyldimethylbenzylammonium chloride, dioleyldimethylammonium chloride, octadecyltrimethylammonium chloride, a alkyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, a octadecylamine acetate, a hexadecylamine acetate, a perfluoroalkyltrimethylammonium salt and a perfluoroalkyl quaternary

ammonium salt.

12. A frosting method using the glass etching liquid composition for a glass surface comprising the steps of:

(a) cleaning a glass surface with a cleaning agent and wiping the glass dry,

(b) protecting the glass surface by masking on to a portion where etching is not required,

(c) coating the glass surface with the glass etching liquid composition as claimed in any one of claims 1,3,4,5,6,7,8,9 and 11 by immersing or spraying to etch the glass surface,

(d) cleaning the glass surface again, and removing the glass etching composition and the masking therefrom.

13. A frosting method using the glass etching gel composition for a glass surface comprising the steps of:

(a) cleaning a glass surface with a cleaning agent and wiping the glass dry,

(b) protecting the glass surface by masking on to a portion where etching is not required,

(c) coating the glass surface with the glass etching gel composition as claimed in any one of claims 2 to 11 by immersing, applying with a brush, or squeezing from a tube to etch the glass surface,

(d) cleaning the glass surface again, and removing the glass etching composition and the masking therefrom.

14. The frosting method for a glass surface as claimed claim 12 or 13, wherein said cleaning agent is selected from water, a

soap, a household cleanser or a household detergent.

15. The frosting method for a glass surface as claimed in any one of claims 12 to 14, wherein said masking is made by an oily pen, an oily paint, a resin paint, an acrylic paint, a masking tape, a seal, a silk screen printing method, or other printing methods.

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## ABSTRACT OF THE DISCLOSURE

A glass etching composition free from health hazard and environmental pollution, and a frosting method using the composition for a glass surface are provided.

# COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, next to my name.

I believe I am the original, first, and sole inventor (if only one name is listed below) or an original, first, and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

GLASS ETCHING COMPOSITION AND METHOD FOR FROSTING  
USING THE SAME

the specification of which:

\_\_\_\_\_ is attached hereto.  
x was filed on 26 April 2000  
as United States Application Number \_\_\_\_\_  
or PCT International Application Number PCT/JP00/02752  
and was amended on \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above. I do not know and do not believe that the claimed invention was ever known or used in the United States of America before my invention thereof, or patented or described in any printed publication in any country before my invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, and that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months (for a utility patent application) or six months (for a design patent application) prior to this application.

I acknowledge the duty to disclose all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d), of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

<u>Prior Foreign Application(s)</u>			<u>Priority Claimed</u>	
<u>11/119510</u>	<u>Japan</u>	<u>27 April 1999</u>	<u>x</u>	
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
_____	_____	_____	Yes	No
(Number)	(Country)	(Day/Month/Year Filed)		
_____	_____	_____	Yes	No
(Number)	(Country)	(Day/Month/Year Filed)		
_____	_____	_____	Yes	No
(Number)	(Country)	(Day/Month/Year Filed)		
_____	_____	_____	Yes	No
(Number)	(Country)	(Day/Month/Year Filed)		

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below

(Application Number)

Filing Date

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Number)

Filing Date

(Status - patented, pending, abandoned)

S- I hereby appoint Mark R. Shanks (33,781), Toni-Juneil Herbert (34,348), Christopher H. Lynt (33,619), Chester T. Barry (40,327), and Maria L. Maebius (42,967) of SHANKS & HERBERT, telephone (703) 683-3600, with a mailing address at:

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with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith.

The undersigned hereby authorizes the U.S. Attorneys named herein to accept and follow instructions from undersigned's assignee, if any, and/or, if the undersigned is not a resident of the United States, the undersigned's domestic attorney, patent attorney or patent agent, as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U. S. attorneys and the undersigned. In the event of a change in the person(s) from whom instructions may be taken, the U.S. attorneys named herein will be so notified by the undersigned.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application of any patent issued thereon.

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